



## Sustainability analysis of innovative technologies for the rare earth elements recovery

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### ABSTRACT

The rare earth elements (REEs) were classified as critical raw materials for Europe for their economic relevance and the supply risk. Currently, most of REE production is concentrated in the Chinese area and it is used for the production of many technologies including: fluorescent lamps, fluid catalytic cracking catalysts and permanent magnets. At the end of their life, these products can cause management problems, mainly due to the hazardous component presence. Nevertheless, this critical issue is combined with the significant content of REEs, which makes them a potential resource of secondary raw materials. In this regard, the literature reports many processes for the waste exploitation, but the effective sustainability is often neglected. In this context, the present paper took into account three processes, one for each mentioned waste, to assess both the environmental and the economic aspects. The obtained results were allocated on the basis of metals market price proving an advantage for most of the elements, compared to the primary production. Following the paper evaluation, the fulfillment of the circular economy approach could reduce up to 200 times the impact in the climate change category and up to 70 times the cost due to the REE mining.

### 1. Introduction

The rare earth elements (REEs) include scandium (Sc), yttrium (Y) and the 15 lanthanide elements of the IUPAC Periodic Table. The relevance of these elements is due to the excellent electronic, optic, magnetic and catalytic properties which give them an important role in emerging clean technologies [1,2]. Nowadays, about the 90% of REE production is concentrated in China, followed by Australia, Russia, India, Brazil, Thailand, Malaysia and Vietnam [3,4]. The global estimated production of REEs was 126,000 t of rare earth oxides (REO) in 2016 and China's Rare Earth Industry Association has forecast that the use of these elements in China will increase to 149,000 t by 2020 [4]. Considering their properties, the REE use includes several applications,

mainly the production of: catalysts (24%), magnets (23%), polishing (12%), batteries (8%) and others. Around 3% of REEs is used for the production of phosphors and pigments [1]. The European Commission has classified this group of elements as critical raw materials for its supply risk, assigning a substitution index higher than 0.9, in a 0–1 range [3]. This parameter confirms the difficulty in metal substitution and it highlights the necessity to develop recycling processes for their recovery from waste, as fluorescent powders, catalyst and permanent magnets [5]. The criticality is confirmed worldwide, since the Chinese control on the metal market, with the consequent quotas and taxes, causes a risk also for the US supply [6]. In this regard, the US Department of energy assessed the criticality of Y and some REEs, in the medium term (up to 2025), including two relevant parameters: the

**Abbreviations:** Ba, Barium; CRT, Cathode ray tubes; Ce, Cerium; CFC, Chlorofluorocarbon; CTUh, Comparative toxic unit for human; CTUe, Comparative toxic unit for environmental; DEHPA, Di-(2-ethylhexyl) phosphoric acid; DCF, Discounted Cash Flow; DCI, discount cash inflow; DCO, discount cash outflow; DPBT, Discounted Payback Time; Eu, Europium; FCCC, Fluid catalytic cracking catalysts; Gd, Gadolinium; Fe, Iron; La, Lanthanum; LCA, Life cycle assessment; LED, Light emission diode; LCD, Liquid crystal display; Hg, Mercury; NdFeB, Neodymium iron boron; NPV, Net Present Value; NMVOC, Non-methane volatile organic compounds; PEF, Product Environmental Footprint; Pr, Praseodymium; PI, Profitability index; Ni, Nickel; REE, Rare earth element; REO, Rare earth oxides; Sc, Scandium; Tb, Terbium; Y, Yttrium; V, Vanadium; WWT, Waste water treatment

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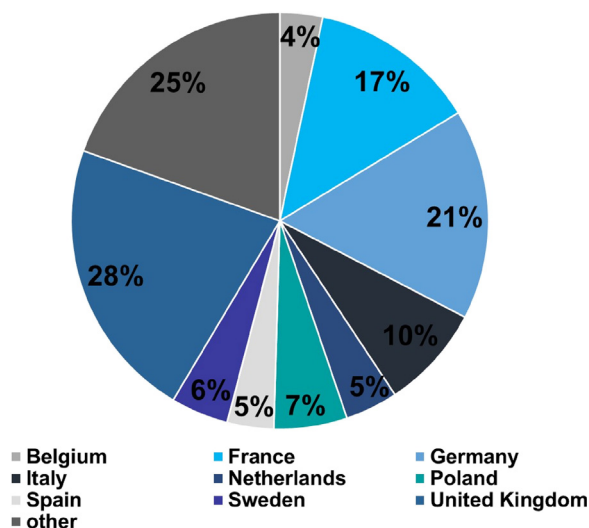


Fig. 1. Contribution of European countries to the WEEE collection in the categories of IT and telecommunications equipment and lighting equipment, at 2016. The contributions lower than 4% are included within “other” [11].

importance to clean energy and the supply risk [7]. In agreement with this result, the National Research Council assigned the highest score 4 to the REE group, related to the supply risk for all the applications [8]. Nevertheless, so far there is no technology for rare earth recovery that goes beyond the proof of concept, there are not economic viable business models, at present.

The interest for the fluorescent powder is due to the strong development of the telecommunications field which has caused a fully replacement of cathode ray tube (CRT) devices and fluorescent lamps by new technologies, like LCDs and LED screens. This technological change can be translated into a flux of about 50,000–150,000 t/year of end-of-life CRTs and more than 50,000 t of lighting equipment collected within Europe, which is not expected to decrease in the next years [9–11]. The significant WEEE amount can be translated into a high cost (both environmental and economic) due to the transport from the producer country to the final treatment. In this regard, United Kingdom, France, Germany and Italy show the greatest contribution to the WEEE collection in the categories of IT and telecommunications equipment and lighting equipment (Fig. 1) [11].

A typical fluorescent lamp contains glass, ferrous materials, and fluorescent powders, which are considered as hazardous waste for the mercury content and they need to be properly handled before the recycling [12,13]. The current treatments allow the recovery of most traditional fractions like glass, metals (filaments, electrodes, and caps), plastics (usually used for the energy production), phosphors and mercury [14,15]. On the other hand, the fluorescent powders are disposed of as dangerous materials, despite their relevant content of REEs. Indeed, as reported by Tkaczyk et al. (2018), this fraction could be a possible source of: Y, Eu, Ce, Tb and Gd, present in phosphors form. According to Wang et al. (2011), the REE content in the phosphors of lamps can reach the 27.9% but only the 10% is currently recovered. The low percentage of REE recovery is due to the high acid resistance of some types of phosphors [16]. Indeed, there are several phosphors in the lamps: the red phosphors  $Y_2O_3:Eu^{3+}$  (YOX), the green phosphors  $LaPO_4:Ce^{3+}, Tb^{3+}$  (LAP),  $(Gd,Mg)B_5O_{12}:Ce^{3+}, Tb^{3+}$  (CBT),  $(Ce,Tb)MgAl_{11}O_{19}$  (CAT) and the blue phosphors  $BaMgAl_{10}O_{17}:Eu^{2+}$  (BAM) [17–19], with different chemical properties.

## 2. Literature review

The scientific literature is rich in recycling processes for the Y and Eu extraction from fluorescent powders in lamps and cathode ray tubes,

but it is still poor of researches for the phosphates treatment combined with the REE recovery, particularly Eu, among the most relevant elements from an economic point of view [2,20,21]. Different hydro-metallurgical approaches were optimized for the REE recovery from fluorescent powder, including solvent extraction [22,23] and the ionic liquid use [24,25]. The metal leaching can be carried out by diluted acids, including sulfuric and hydrochloric [12,26–33]. These agents allow the red phosphors dissolution, whereas, strong acid conditions are necessary for the reaction with green phosphors for their high chemical resistance. In this regard, Wang et al. (2011) describe a treatment with a 4 M hydrochloric acid solution, in the presence of hydrogen peroxide (4.4 g/L) which allows the extraction of rare earth trichromatic phosphors containing Y, Ce, Eu, Tb and La [16]. Alternatively, a mechanical activation by ball milling, to destroy the crystal structure of the green and blue phosphors [34,35], or a preliminary alkaline fusion [12,27,30,36] can be performed to transform the phosphors into oxides, which can be easily dissolved by diluted acid media. The leaching step is followed by a precipitation and/or a solvent extraction to obtain a REEs rich product.

Considering the high raw material consumption and the selected operative conditions, most processes are not yet sustainable from an economic point of view; nevertheless, the study of the technological innovation confirms the actual interest towards the application on a real scale [37]. In this regards, Table 1 reports several patents related to the fluorescent powder exploitation for the REE recovery.

Spent fluid catalytic cracking catalysts (FCCC) represent another potential secondary source of REEs, mainly La. These metals are used to control the activity and the selectivity of the zeolite in oil refining cracking processes. The catalysts demand is increasing in the recent years with the consequent production of significant waste flows to manage [20]. Spent FCCC can be industrially managed for metal recovery, regenerated for a reuse or disposed in landfilling sites. The first option could allow an economic advantage, nevertheless, it produces high quantity of hazardous waste and significant environmental impacts. On the other hand, the possible regeneration can be applied for a limited number of times and it is not possible for all the catalytic system. It is evident that the landfilling option causes the high value fraction loss, combined with a negative environmental effect [38]. Currently, the main techniques of end-of-life FCCC recycling include the production of cement and ceramic materials, wastewater filtering agent and asphalt mixtures, thanks to their intrinsic characteristics [20,39–44]. Minor applications consist of their use as catalysts for plastic and biomass pyrolysis/gasification or for the synthetic fuel production [45–47]. Nevertheless, these processes have not been widely developed at industrial scale and the exploited fraction is still low, if compared with the high annual quantity that reach the collection center [48]. Therefore, the disposal in landfilling sites or the use for concrete blend is still the main choice for the spent catalyst management, despite the content of REEs and possible valuable metals, like V and Ni, potentially recoverable. La and Ce concentration has gradually increased over the years, and the current average is between 3% and 5%wt, as oxides [49].

The scientific literature proposes different approaches for the REE recovery from this waste, including a leaching followed by a solvent extraction [50–52], or precipitation [53,54]. On the other hand, a limited number of published patents can be found at present, confirming that the field of REE recovery from spent FCCC is in development (Table 1). The main barrier for Ce and La recovery from FCCC is not technical but economic, as the rare earth prices, coupled with their low concentration in FCCC, make any process currently unprofitable [49].

The permanent magnets represent another representative example of REE application [55]. These components are the key component of hybrid electric vehicles, they are playing a crucial role in the electric power technologies based on renewable sources, and they are used in the hard disk drives of personal computers. However, no recycling has

**Table 1**  
Patents related to the REE recovery from FCCC, fluorescent powders and permanent magnets.

Title	Patent number	Year	Reference
<b>FCCC</b>			
Recycling method of vanadium-containing waste FCC equilibrium catalyst	CN105251525	2016	[63]
Process for recovering rare earth metals	WO2014020626	2014	[64]
Process for metal recovery from catalyst waste	WO2012082597	2012	[65]
<b>Fluorescent powder</b>			
The method of producing red fluorescent powder from waste fluorescent powder	TW201638295	2016	[66]
Process for recovery of yttrium and europium from lamp phosphor waste	WO2016065433	2016	[67]
Method for recycling rare earth element yttrium from waste fluorescent powder	CN106191446	2016	[68]
Method for recycling zinc in waste cathode-ray tube fluorescent powder and enriching rare earth on basis of self-propagating reaction	CN105755288	2016	[69]
Method for recycling rare earth from waste fluorescent powder	CN105568005	2016	[70]
Method for preparing rare-earth fluorescent up-conversion material by use of waste fluorescent powder	CN104388087	2015	[71]
Method for recycling rare earth metal from waste fluorescent powder	CN105087934	2015	[71]
Method of high-effectively recycling rare earth from waste CRT fluorescent powder	CN105039698	2015	[72]
Method for effectively recycling rear earth elements in fluorescent powder waste material	CN103667709	2014	[73]
Comprehensive recycling treatment method of waste rare-earth fluorescent lamp	CN103627906	2014	[74]
Method for recycling rare earth elements in rare earth fluorescent powder waste by ultrasonic-submolten salt process	CN102828030	2012	[75]
Method for recycling rare earths from cathode-ray tube fluorescent powder	CN102796872	2012	[76]
Method for recycling rear-earth elements from abandoned fluorescent lamps	CN102634667	2012	[77]
A method for the recycling fluorescent powder of scrap cathode ray tube	TW200916552	2009	[78]
Method for recovering fluorescent powder	JP2004262978	2004	[79]
<b>Permanent Magnets</b>			
Preparation method of regenerative sintered neodymium-iron-boron permanent magnet	CN106971802	2017	[80]
Method for preparing high-performance permanent magnet via diffusion permeation treatment of sintered neodymium iron boron recycled waste materials	CN106158339	2016	[81]
Recycling method for recycled waste material of sintered neodymium iron boron	CN105931781	2016	[82]

been carried out, until now: devices (electric vehicles and wind turbines) have still not reached significantly their end of life, and hard disk drives are not separated from the computers by WEEE recyclers, being shredded and disposed. Nevertheless, the recycling of spent high performance NdFeB permanent magnets is currently becoming of high interest, due to the significant content of strategically important REEs. The NdFeB material use is due to its high magnetic strength, the inexpensive matrix material (iron) and the suitable stability, if compared to the available alternatives [5]. The magnets contain mainly Nd and Pr (around 23% and 69% of the whole REEs content, respectively), with valuable impurities as Dy, Tb and Gd, variable on the basis of the specific application [2]. The literature reports different approaches for the recovery including: hydrometallurgical, pyrometallurgical, electrochemical and the combination of these treatments [5,56,57]. The first option includes an acid leaching followed by precipitation [58] or solvent extraction [22,57,59,60]. Among pyrometallurgical processes, different possibilities are reported in the literature, including liquid molten extraction [61] and hydrogenation [62]. Overall, all the cited techniques need a high raw material consumption with a negative effect on the economic cost and they are still far from an application on a real scale, as also confirmed by the low number of available patents (Table 1).

Overall, the study of the most recent scientific literature, combined with the published patents, suggests that fluorescent powders, FCCC and permanent magnets represent promising sources of secondary REEs, in the perspective of a circular economy. Nowadays, there are not consolidated technologies, suitable for the implementation on a real scale and the reason can be found in the high environmental load, often translated into a significant economic impact. On the other hand, the development of high sustainability recycling strategies could represent an economic opportunity [83]. The possibility to implement innovative facilities, could support the current processes carried out by few companies on the European territory, with a strong impact mainly due to the waste transport for high distances [83,84]. In this context, the present paper analyzed three innovative recycling processes, evaluating both the environmental and the economic sustainability aspects. In agreement with the literature, the life cycle assessment (LCA) was selected as a tool for the environmental evaluation. The approach is one of the most powerful to identify the real potential of innovative

technologies, in terms of environmental sustainability, if compared with the best-established options [85]. Furthermore, this method was proved to be an excellent tool to assess the WEEE recycling treatment, to improve the sustainability of the process conditions and to drive the decision makers towards low environmental impact strategies of electronic waste management [86–96]. Similarly, the economic sustainability of the processes can't be neglected, since the economic criteria usually drive the recycling strategies in a real context. This was assessed through the estimation of fixed and operating costs and through the profitability analysis of the three recycling processes. In this case, the Discounted Cash Flow (DCF) method was applied, as a well-known economic assessment method that estimates the attractiveness of an investment; this is a reliable approach that is also recommended by the European Commission as reference method for the evaluation and comparison of different investment opportunities [97].

### 3. Materials and methods

#### 3.1. Process description

The present section describes the innovative processes considered for both the environmental and the economic assessment. The description is combined with the energy and the mass balances, referred to a functional unit of 1 kg of treated waste.

##### 3.1.1. Fluorescent powder recycling

The fluorescent powder recycling process follows the conditions described by Ippolito et al. (2017), improving the calcination step which avoids the Ba(OH)<sub>2</sub> use. More in detail, the process includes (Fig. 2): a thermal treatment, a sulfuric acid leaching for the REE extraction, the recovery of REE oxalates by a precipitation with oxalic acid, followed by a calcination to obtain REE oxides and a wastewater treatment (WWT).

The preliminary thermal pre-treatment, carried out at 950 °C for 1 h, aims at the transformation of rare earth phosphates into rare earth oxides, promoting the following leaching. Furthermore, it allows to solve one of the most critical issue of the spent fluorescent lamps management due to the Hg presence [25]. The metal vaporization, with the consequent removal, decreases the risk connected with the

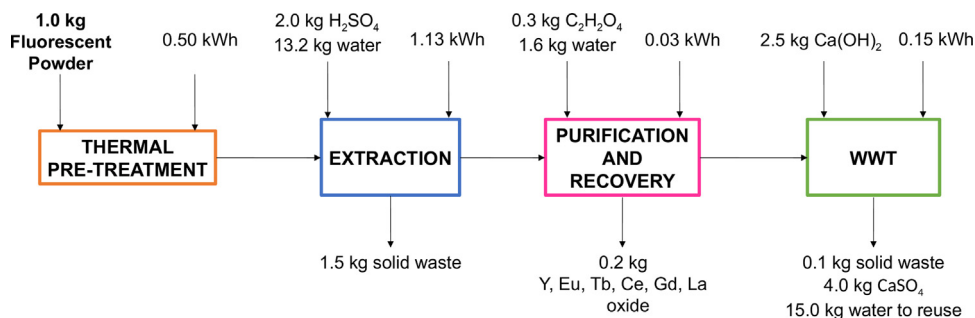


Fig. 2. Block diagram of the fluorescent powder innovative recycling process. (Functional unit: 1 kg of treated waste).

fluorescent powder disposal. Considering an industrial scale, this section should be designed including a system for the hazardous emissions treatment (e.g. cooling and activated carbons). As concern the leaching stage, the process is carried out by 2 M  $\text{H}_2\text{SO}_4$  solution, at 10%wt/vol. concentration, at 50 °C, under stirring, for 2 h. The treatment allows to achieve extraction efficiencies of: 90% for Y and Eu, 65% for Tb, 45% for Ce and Gd and 30% for La. The filtration of the resulting solution produces: a solid residue, to wash with water and dispose of as hazardous waste, and the leach liquor to treat with oxalic acid for the REE precipitation. This agent is added in stoichiometric amount with 10% of excess, at room temperature, for 1 h. Thereafter, the REES oxalates are calcined at 600 °C, for 1 h obtaining a mixture of REEs. The product is composed of: 82% of Y, 8% of Eu, 2% of Ce, 2% of Gd, 2% of La and 2% of Tb, with an overall REE oxide purity higher than 98%. The spent acid solution from oxalic acid precipitation is sent to WWT which includes: a first step with lime solution (20%w/w) to obtain a precipitate, rich in calcium sulfate, and a purification stage, adding lime up to pH 8–9. The recovered water can be partially recirculated within the process, whereas the remaining portion is discharged into the industrial sewage network.

### 3.1.2. FCCC recycling

As described by Ferella et al. (2018), the FCCC recycling process is composed of five main stages (Fig. 3): a REEs extraction by sulfuric acid leaching, precipitation and recovery of REEs sulphates, zeolite synthesis, recovery of spent acid and WWT [48].

The leaching stage is carried out by 1.84 M  $\text{H}_2\text{SO}_4$  solution, at 15% wt/vol. concentration, at 80 °C, under stirring, for 2 h. After filtration, the solid residue is washed with water until pH 6–6.5 is reached in the washing water. The leaching treatment is followed by the purification and the recovery. More in detail, the pH of the leach liquor is raised up

to pH 2, by 50%wt NaOH solution, with the consequent precipitation of white REE sulphates. The product is composed of: 81% of  $\text{La}_2(\text{SO}_4)_3$ , 6% of  $\text{Ce}_2(\text{SO}_4)_3$  and 13% of  $\text{Al}_2(\text{SO}_4)_3$ , an impurity due to the high Al solubility. Such sulphates are recovered by filtration and washed with water, thus dried and sold for further refining and separation of La and Ce. Currently, the sole recovery of La and Ce from spent FCCC is not profitable, as the main material is represented by the solid residue from the extraction stage. Therefore, the exploitation of this waste, to produce a synthetic zeolite, useful for several applications (e.g. adsorption of metals and/or organic compounds from wastewaters and waste solutions, catalyst carrier) increases the process sustainability [48]. In this regard, the washed solid residue from leaching is mixed with at least the same amount by weight of powdered NaOH, and roasted at 600–650 °C for 1.5 h. The resulting material is crushed and mixed with water at room temperature for 8 h, and further 12 h at 85 °C, under stirring. Thereafter, the zeolite completes the synthesis, hence it can be washed by water at pH 7–7.5 and dried at 105 °C. The spent acid solution, separated from the solid leaching residue, shows an acid pH, suitable to be recirculated, within the extraction step, after a nanofiltration and a refresh using a small amount of concentrated  $\text{H}_2\text{SO}_4$ . The nanofiltration produces also a retentate, around 20% of the inlet flow, to send to the WWT, mixed with wastewater streams from washing, filtration of REEs sulphates and zeolite. This flow decreases the pH value within the WWT section (around 8), where the alkaline conditions are due to the spent solution from the zeolite production. Concentrated  $\text{H}_2\text{SO}_4$  and 20%wt/vol. lime solutions can be added for a fine pH regulation, if necessary. The recovered water can be partially reused in the process, whereas the remaining portion is discharged into the industrial sewage network.

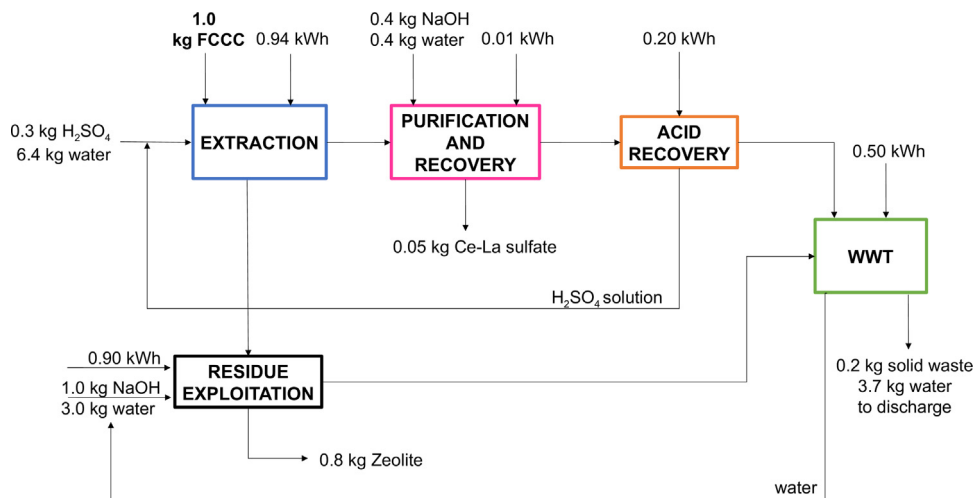


Fig. 3. Block diagram of the FCCC innovative recycling process. (Functional unit: 1 kg of treated waste).



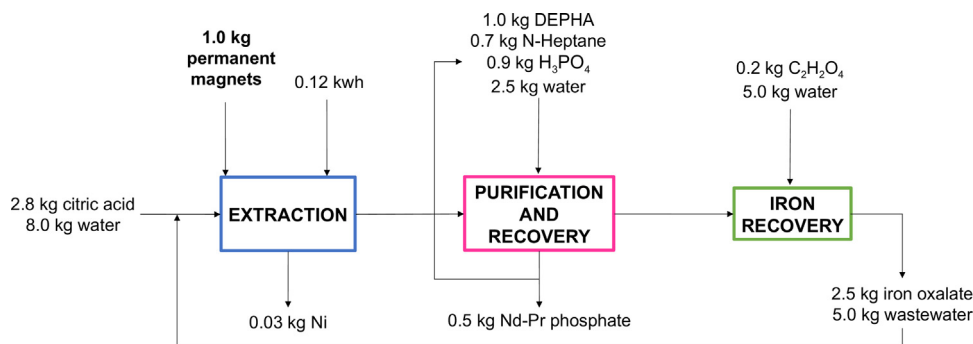


Fig. 4. Block diagram of the permanent magnet innovative recycling process. (Functional unit: 1 kg of treated waste).

### 3.1.3. Permanent magnet recycling

The permanent magnet process considered for the assessment follows the details described by Birloaga and Vegliò (2018) patent (Fig. 4) and it includes: the REEs leaching by citric acid, a purification and recovery step, carried out by solvent extraction followed by stripping and precipitation of Nd and Pr phosphate, and the iron recovery in oxalate form [98].

More in detail, the leaching of the powder from a manual and mechanical pre-treatment, is achieved by a 10% wt./vol. citric acid solution, under stirring, at room temperature, for 3 h. The obtained solution is filtered under vacuum conditions and the resulting solid, with a Ni content higher than 60%, is further washed. The exploitation of Ni content allows a double advantage due to both the metal recovery and the avoided disposal of the waste, classified as carcinogenic.

The solution from solid residue washing has a high concentration of Nd, Pr and Fe, therefore, it is mixed with the leach liqueur and it is sent to the solvent extraction section. This step uses the organic solvent Di-(2-ethylhexyl)phosphoric acid (DEHPA), diluted in n-Heptane, at a concentration of 50%vol./vol. The reaction takes place at room temperature, for 15–20 min, under stirring. The following recovery involves the organic phase stripping by phosphoric acid for 1–2 h, under stirring. The step efficiency reaches the 98% with the final recovery of Nd and Pr phosphate (the 78% and the 22% of the whole product, respectively). Furthermore, the 95% of both the organic and the aqueous fractions can be recirculated for further treatments. The addition of oxalic acid, with a concentration of 20% wt./vol., to the aqueous solution achieved within the solvent extraction allows the iron oxalate recovery. The reaction carries out at room temperature, for 1–2 h and the obtained precipitate is filtered. The separated solution is suitable for the recirculation, after a 10% of refresh, for further leaching processes.

## 3.2. Life cycle assessment

### 3.2.1. Goal and scope definition

The LCA took into account three processes for the recovery of REEs from: fluorescent powders, FCCC and permanent magnets. The functional unit selected for the assessment is 1 kg of each waste, previously disassembled and possibly shredded, following the traditional treatments, as described below. The choice is due to the simple definition, measurability and reproducibility of this quantity, in agreement with the LCA ISO standard 14040 and 14044:2006 [99,100]. The analysis aimed at the quantification of the environmental burden of the process steps, in the highest quality impact categories, with the identification of the main weaknesses to improve. Furthermore, the normalization and weighting phases allowed to recognize the most critical categories for each treatment. To define the processes sustainability, the carbon footprint of the treatments was compared with the carbon dioxide equivalent due to the primary production of the recovered REEs. Considering the several recovered metals for each process, the environmental load was allocated based on the economic value on the market.

The overall system boundaries, summarized in Fig. 5, consider: the

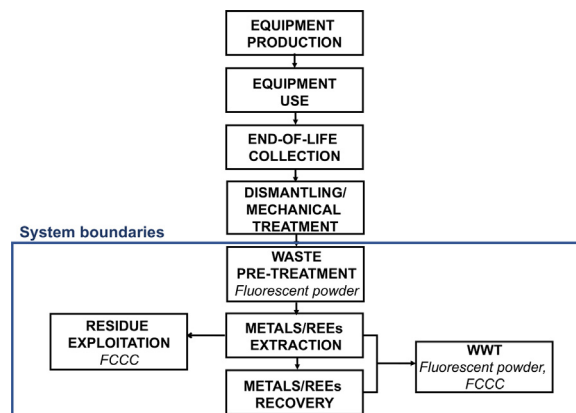


Fig. 5. System boundary for LCA analysis of the three considered treatments for the REEs recovery from fluorescent powder, FCCC and permanent magnet.

waste treatment for the REEs and metal recovery, including also a pre-treatment for the fluorescent powder, the WWT for the fluorescent powder and the FCCC and a further residue exploitation for the FCCC. On the other hand, materials and energy flows related to the equipment life (production and use), the waste collection and dismantling/mechanical treatment were excluded. More in details, the processes for the preparation for the following exploitation are different for each waste. The fluorescent powder is produced by the traditional treatments for the end-of-life lamps, currently operated within conventional recycling plants. On the other hand, the FCCC do not need specific treatments, since the product is already pulverized, with a grain size around 80  $\mu\text{m}$ , without a significant organic content.

The permanent magnets used for the analyzed treatment are manually disassembled from the hard disk drives of the exhausted personal computer and the sintered permanent NdFeB magnets are further immersed in a muffle furnace, at about 320  $^{\circ}\text{C}$ , for 1–2 h. After cooling, they are milled with a planetary ball mill.

Some assumptions, described below, were necessary to carry out the analysis. The positive effect of the recovery of secondary raw materials were quantified as avoided impacts for the primary production and reported as negative values. In this regard, considering the data availability, the credit due to the zeolite production, within the FCCC exploitation, is related to the calcium silicate.

On the other hand, considering the low quantity of Ni obtained by the permanent magnet treatment, compared to the other products, this environmental gain was excluded from the assessment. Another assumption related to this process is that about the organic waste flow from the purification and recovery step (the 5% which is not recovered). Following the literature information, this kind of streams is incinerated and its effect on the health is lower than the most part of the organic solvent [101]. Therefore, the process selected for the LCA analysis is a hazardous waste flow, rich in carbon.

In order to fill the information gap related to the oxalic and the citric acids production, within the Gabi Database, these processes were built following the details described by Santoro et al. (1999) and Murad and Khalaf (2003), respectively.

More in detail, oxalic acid is produced by *Aspergillus niger* fermentation, using milk whey as carbon source (with a concentration of 100 g/L), a culture temperature at 30 °C, shaking at 150 rpm. The fermentation is carried out for 14 days and the pH was restored to 6 value with concentrated NaOH, each day. At these conditions, a final oxalic acid concentration of 37 g/L, with a maximum production rate of 3.4 g/L-d, is obtained [102].

Similarly, citric acid is produced by *Aspergillus niger* fermentation, at the same conditions chosen for the oxalic acid, using soy whey as carbon source. The maintenance of the pH 3, adding concentrated NaOH each day, allows the enhancement of the acid production, with a final concentration around 90 g/L [103,104]. Considering the resulting citric acid concentration, three times higher than the oxalic one, with a comparable raw material consumption, the environmental load due to its production is assumed to be one third of that caused by the oxalic acid production.

As concern the electricity production, the considered processes are based on European average, including electricity own consumption, transmission/distribution losses of low voltage electricity supply and electricity imports from neighbouring countries.

### 3.2.2. Software for LCA

The thinkstep GaBi software-System and Database for Life Cycle Engineering (compilation 7.3.3.153; DB version 6.115) were used for the production processes of energy and raw materials and the quantification of the environmental burdens of the three analyzed processes. The impact categories and the related characterization methods were selected in agreement with the Product Environmental Footprint (PEF) guidelines and the ILCD recommendations. A further normalization and weighting step allowed the determination of the relevance of the different environmental impact categories for person equivalent.

## 3.3. Cost analysis

### 3.3.1. Goal and scope definition

Considering the possible scale-up of the described processes, the economic assessment aimed at the estimation of the costs due to the facility implementation. Therefore, the analysis included the investments for six main aspects: the raw materials, the waste treatment and disposal, the utilities, the laboratory and quality check, the facility dependents and the labor dependents. The selected functional unit for both the fluorescent powders and FCCC is 4000 t/year, chosen as the possible recycling plant capacity. On the other hand, 1580 t/year of permanent magnets was considered since they are achieved through the disassembly of 72,000 t of Hard Disk Drives.

The plant capacities studied in this work are typical of medium-large firms; they have been chosen considering the amount of the three spent materials, i.e. FCC catalysts, hard disks and fluorescent lamps that are collected annually in Italy and nearby countries. Hence, this study is applicable to the market of European Union and the relevant collection/recycling schemes.

It is evident that the economic elaboration represents a prevision and further possible costs could not be included. Nevertheless, it represents an essential starting point to identify the most significant plant weaknesses and to estimate the effective recycling treatment convenience, if compared with the traditional primary metal production. In this regard, the cost for kg of each product, allocated by the market price criteria, was compared with the current quotation.

### 3.3.2. Software for economic assessment

The SuperPro Designer v9.5 (Intelligen, USA) software was used for the cost estimation for the treatment of: fluorescent powders, FCCC and

permanent magnets.

### 3.3.3. Profitability analysis

Profitability analysis has been carried out through the DCF method, with the following hypotheses:

- cash inflows and outflows are the only ones considered in the analysis of the recycling plants;
- the calculation of the investment's cash flows is based on an incremental approach;
- the aggregation of occurring cash flows during different years requires the adoption of an appropriate discount rate.

Nevertheless, a critical point of the method is that its reliability completely depends on the level of confidence of the future cash flows. There are several indexes currently used by economists for the assessment of the profitability of an investment. Nevertheless, net and gross profit, although commonly used by the experts, do not analyze all the lifetime of an investment, but a pre-defined period only. For that reason, in this work authors preferred the Net Present Value (NPV) and the Discounted Payback Time (DPBT). The NPV is defined as the sum of present values of individual cash flows:

$$NPV = \frac{\sum_{t=0}^n (DCI_t - DCO_t)}{(1+r)^t} \quad (1)$$

where  $DCI_t$  is the discount cash inflow (€),  $DCO_t$  is the discount cash outflow (€),  $r$  is the opportunity cost of capital (%) and  $t$  is the period time (years).

The DPBT represents the number of years required to balance the cumulative discounted cash flows and the initial investment:

$$\frac{\sum_{t=0}^{DPBT} (DCI_t - DCO_t)}{(1+r)^t} = 0 \quad (2)$$

where, as already written,  $DCI_t$  is the discount cash inflow (€),  $DCO_t$  is the discount cash outflow (€),  $r$  is the opportunity cost of capital (%) and  $t$  is the period time (years).

The computation of such indexes and DCF is shown elsewhere [83,97]. Projects that present significant difference among values of investment costs can be investigated through another index, known as profitability index (PI), that is coherent with NPV. It is calculated as follows:

$$PI = \frac{NPV}{Investment} \quad (3)$$

where NPV is the Net Present Value (€) and the Investment is the capital invested for the construction of the plant (€). Since the numerator of this index is the NPV, the condition of profitability is satisfied when  $NPV > 0$ .

For the profitability analysis of the three case studies, the following common input data were used: project lifetime 15 years, interest rate 3%, inflation rate 1%, opportunity cost of capital 5%, taxes 40% on gross profit, loan period 5 years [83,97]. The following plant capacities were used as input data: 4000 t/year of spent FCCC and fluorescent powders and 1580 t/year of permanent magnets.

### 3.3.4. Scenario analysis

Sensitivity analysis measures the variation of a single variable, while scenario analysis regards the change of more variables. Since the profitability of the three plants was assessed in a baseline scenario related to some hypotheses made on input variables, other cases were assessed as a variation of the expected economic results could occur in the future. A sensitivity analysis was carried out on two critical items, in particular revenues and operating costs. The application of the sensitivity analysis certainly contributes to a better assessment of the investments, since it introduces the variation of specific economic key

**Table 2**  
Alternative economic scenarios assessed for each of the recycling processes.

Scenario	Operating costs	Revenues
A	– 10%	– 10%
B	– 10%	+ 10%
C	+ 10%	– 10%
D	+ 10%	+ 10%

variables, that could occur in the future [83]. For instance, these variables are the price of base metals, REEs and zeolites, that have a direct consequence on the plant revenues. The raw material prices could also change, as well as the cost of oil and consequently natural gas and electricity; also other items could increase, resulting in a growth of the operating costs.

Revenues differ from one process to another. The outputs of the FCCC recycling plant are synthetic zeolite and RE sulphates; moreover, the tipping fee is also included in the total revenues. As regards the other two processes, RE mixed oxides are the sole revenue from the fluorescent powder recycling, whereas the permanent magnets plant produces nickel, Nd-Pr phosphates and iron oxalate as main products. The operating costs taken into account in the economic analysis were purchasing of raw materials, labor-dependent and facility-dependent costs, laboratory and quality control, consumables, waste treatment and disposal, utilities (natural gas and electricity), insurances, maintenance, transportation and finally advertising and running royalties, if any. Four alternative scenarios were assessed, as indicated in Table 2.

The percentages in Table 2 are referred to the values of the baseline scenario operating costs and revenues, listed in Table 5.

## 4. Results and discussion

### 4.1. Life cycle assessment

Table 3 summarizes the process impact obtained by the classification and characterization steps of the LCA analysis, considering all the phases of each treatment. The results exclude the avoided impact due to the REE recovery, which is evaluated at the end of present paragraph.

As concerns the fluorescent powders, the assessment shows an environmental credit higher than the impact in the category of eutrophication freshwater thanks to both the recovery of the calcium sulfate, by the WWT, and the possibility to exploit a scrap for the oxalic acid production. Overall, the extraction is the most critical step, mainly for the residual cake production, classified as hazardous waste.

On the other hand, the greatest impact of the FCCC treatment is due to the residue exploitation step, in most of categories, with a sodium hydroxide contribution around 40–45%. Human toxicity (both cancer

and non-cancer effects) is an exception, since it is almost completely due to the treatment of the solid waste from the WWT.

The evaluation of permanent magnet process impact brought to light the wastewater criticality (in the categories of: climate change, eutrophication freshwater, marine and terrestrial, human toxicity cancer and non-cancer effects), mainly the organic stream from the purification and recovery phase, highlighting the relevance of the re-circulation system, which decreases the flow amount up to 5% of the input. The possibility to produce oxalic acid from a waste substrate is emphasized in the category of eutrophication freshwater, nevertheless, the high electricity consumption causes the greatest acid contribution in many categories. On the other hand, the high environmental load in the categories of ozone depletion and resource depletion, mineral, fossils and renewables is due to the organic solvent use.

The normalization and weighting steps identified the most affected categories for each described treatment (Fig. 6). Fluorescent powder process causes the greatest impact in the categories of: climate change, ionizing radiation and resource, energy carriers the 30%, 25% and 20% of the whole environmental load, respectively. The management of the residual cake, classified as hazardous waste, the calcium hydroxide and the electricity consumption, for both the treatment and the oxalic acid production, are the leading contribution in the three categories. Nevertheless, the environmental impact is partially balanced by the credit in the category of resource, mineral and metals, thanks to the calcium sulfate recovery.

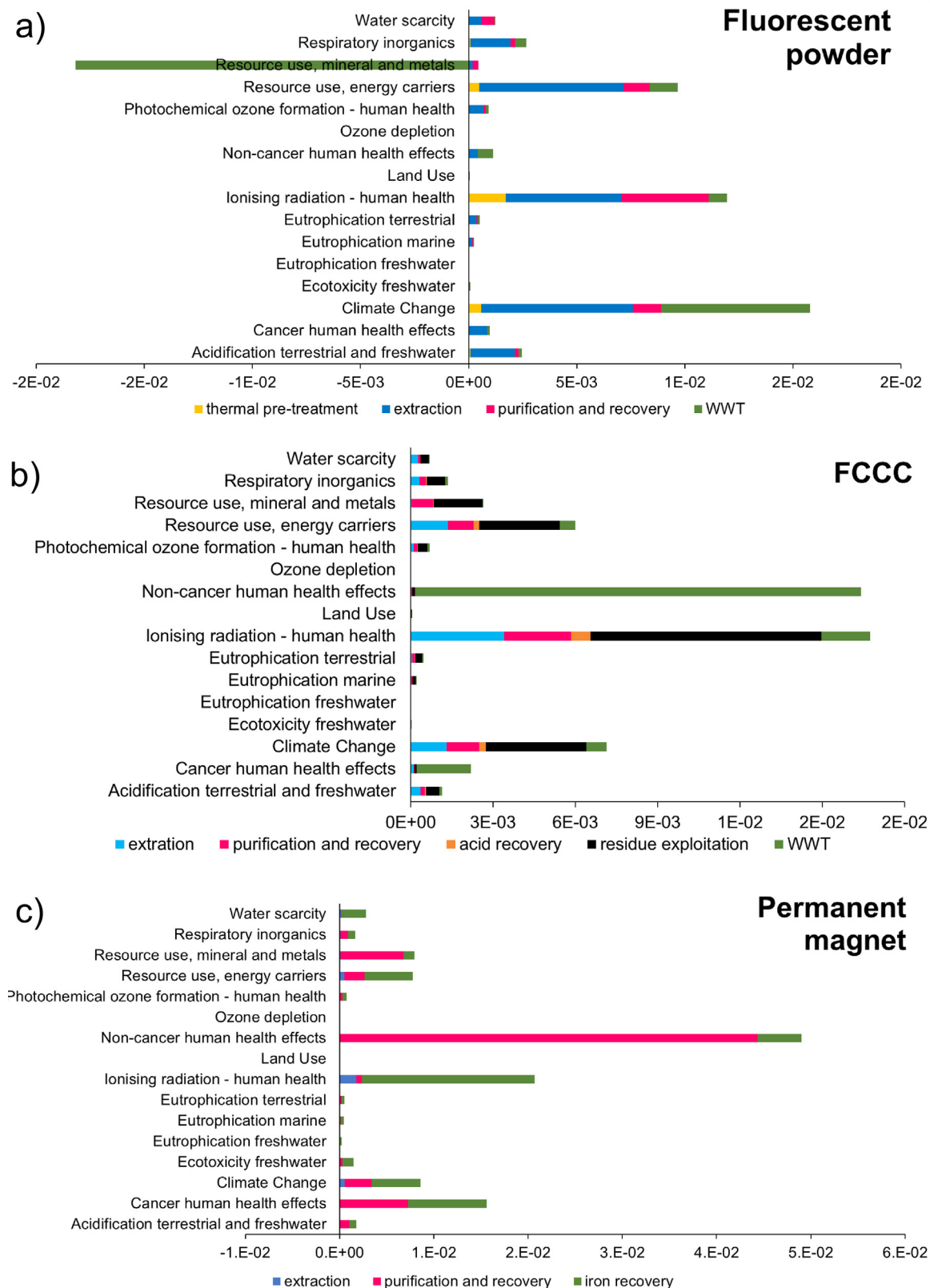
On the other hand, non-cancer human health and ionizing radiation are the most critical categories for the FCCC treatment, mainly due to the WWT and the residue exploitation, respectively. More in details, the production of a solid waste causes about the whole effect of the wastewater process. The electricity consumption and the sodium hydroxide use, are the main weaknesses of the residue exploitation step, contributing with an environmental load of 60% and 30% of the whole phase, respectively.

The most relevant result for the permanent magnet treatment in that related to the non-cancer human health category, with a contribution of the purification and recovery step around the 90%, almost completely due to the organic waste flow. This result confirms the essential effect of the waste flow recirculation.

Considering the relevance of the recovered metals for the manufacture of technological equipment and the necessity of their production, the comparison between the impact due to the recycling process and their primary production is an essential information (Table 4). With this aim, the carbon footprint was chosen as sustainability indicator. The emissions of the treatments: 16 kg CO<sub>2</sub>-eq./kg of REEs for the fluorescent powders, 5 kg CO<sub>2</sub>-eq./kg of REEs for FCCC and 6 kg CO<sub>2</sub>-eq./kg of REEs for permanent magnets were allocated on the basis of the market price [105]. Following this approach, the possibility of REE

**Table 3**  
Results of classification and characterization steps of LCA. (Functional unit: 1 kg of treated waste).

Impact category	Fluorescent powder	FCCC	Permanent magnet
Acidification [mmol of H <sup>+</sup> eq.]	20	10	16
Climate change [kg CO <sub>2</sub> eq.]	4	2	3
Ecotoxicity freshwater [CTUe]	0.4	0.2	9
Eutrophication freshwater [mg P eq.]	– 10	10	150
Eutrophication marine [g N eq.]	2	2	4
Eutrophication terrestrial [mmole of N eq.]	20	20	20
Human toxicity, cancer effects [CTUh·10 <sup>–8</sup> ]	2	4	30
Human toxicity, non-cancer effects [CTUh·10 <sup>–5</sup> ]	0.02	0.4	1
Ionizing radiation, human health [kBq U235 eq.]	0.7	1	1
Land use [kg C deficit eq.]	1	1	1
Ozone depletion [ng CFC-11 eq.]	6	9	130
Particulate matter/Respiratory inorganics [g PM2.5 eq.]	1	0.5	0.7
Photochemical ozone formation, human health [g NMVOC eq.]	7	6	6
Resource depletion water [m <sup>3</sup> eq.]	0.1	0.1	0.2
Resource depletion, mineral, fossils and renewables, [mg Sb eq.]	9	9	180



**Fig. 6.** Results of normalization and weighting steps of LCA, related to: a) fluorescent powder, b) FCCC and c) permanent magnet treatment. (Functional unit: 1 kg of treated waste).

recovery decreases the impact for the metal production up to 200 times, compared with the production from mining [106].

The FCCC treatment represents an exception with a double impact compared with the primary production. This outcome was expected,

due to the relatively low concentration of La and Ce. Nevertheless, this result could be balanced by the avoided disposal of FCCC, classified as hazardous waste for the metal content (mainly Ni and V, around 4000 and 1500 ppm, respectively [49]).



**Table 4**

Comparison between the carbon footprint of metals from the described recovery processes (allocated on the basis of the market price) and that related to the same elements from the primary production.

Metal target	Carbon footprint of metals from secondary production (kg CO <sub>2</sub> eq./kg metal)	Carbon footprint of metals from primary production (kg CO <sub>2</sub> eq./kg metal)
Fluorescent powder process		
Y	0.1	15
Eu	2	395
Ce	0.1	13
Gd	0.9	47
La	0.1	11
Tb	13	297
FCCC process		
La	24	11
Ce	24	13
Permanent magnet process		
Nd	3	18
Pr	3	19

#### 4.2. Economic assessment

The combination of the economic and the environmental results is essential to assess the real benefit of the REE production by the described recycling approaches. In this regard, Table 5 summarizes the cost of the three processes including: the total investment (referred to the facility building and engineering, the specific equipment, the contractor's fee and the contingency) and the operating costs (e.g. raw materials, laboratory- and facility-dependent, waste treatment and disposal, etc.), expressed as €/year. The comparison among the treatments is not possible since the metals recovered amount and the economic value are considerably different. Nevertheless, an interesting information is that about the total investment cost distribution. In this regard, fluorescent powder and FCCC treatments show a most significant cost (70% and 80%, respectively) due to the fixed capital (evaluated by Superpro software, including the costs for: equipment purchase and installation, piping, instrumentation, electrical facilities, insulation, yard improvement, buildings, auxiliary facilities, engineering & construction, contractor's fee and contingencies). On the other hand, the working capital (which consists of costs for: labor, raw materials, utilities and waste disposal/treatment) is the main investment (around the 80%) for the permanent magnet recovery, since complex dismantling operations are necessary before the metal recovery.

Further results are summarized in Fig. 7, where the different contributions of the operating cost are explained. It is evident that the primary cost, 31–57% of the whole economic load, is due to the raw material purchase, followed by the waste treatment. The economic information is essential to identify the steps to improve for a greater process sustainability and it enhances the significant effect of the waste flows recirculation within the same treatments, in agreement with the environmental results. This possible advantage is mainly evident for the permanent magnet process, where the reuse of the output solution from the purification and recovery step decreases the raw material

**Table 5**

Results of economic assessment, hypothesizing a plant capacity of 4000 tonn/year for the fluorescent powder and FCCC processes and 1580 t/year (from disassembly of 72,000 t of Hard Disk Drives) for the permanent magnet treatment.

	Fluorescent powder	FCCC	Permanent magnet
Total investment cost (€)	2200,000	3000,000	2200,000
Operating costs, including depreciation (€/year)	6700,000	5000,000	22,100,000
Revenues (€/year)	8000,000	6300,000	39,000,000
Recovered metals (tonn/year)	800 (REEs oxides)	180 (La/Ce sulphates)	27 (Ni) 1150 (Nd/Pr phosphate) 4000 (Fe oxalate)

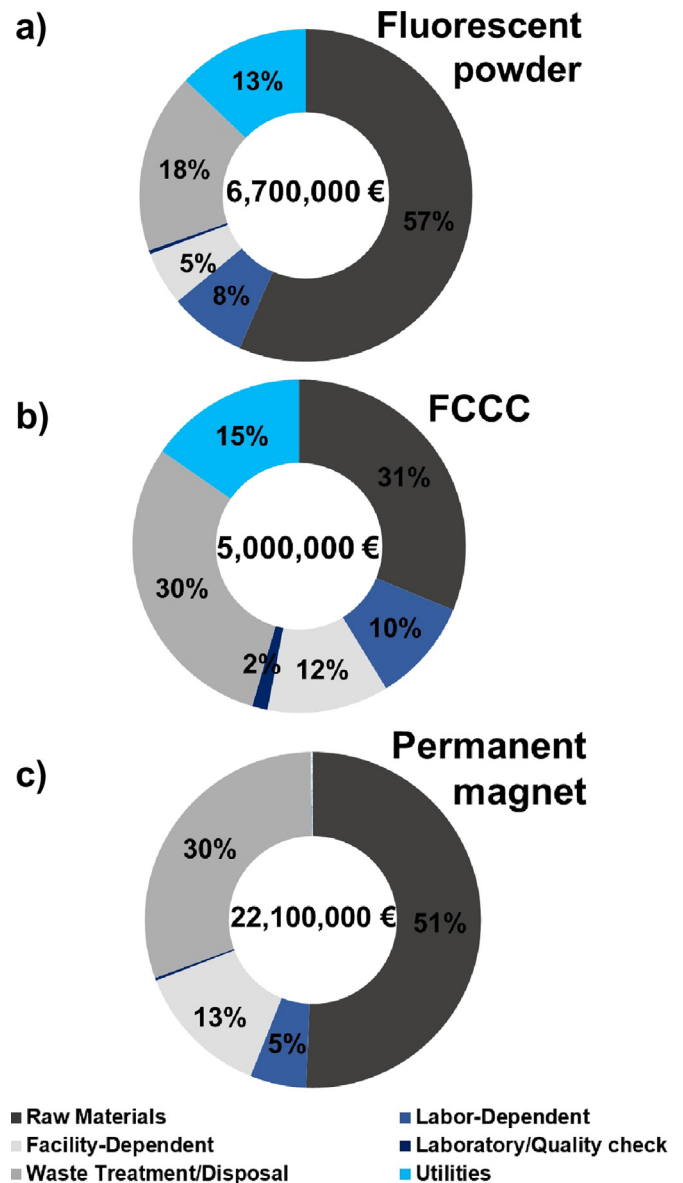


Fig. 7. Main contributions of operating cost for REEs recovery process from a) fluorescent powder, b) FCCC, (plant capacity 4000 tonn/year for both the wastes) and c) permanent magnet (plant capacity of 1580 t/year from the disassembly of 72,000 t of Hard Disk Drives).

consumption up to the 95%. The overall effect is evident since N-Heptane, phosphoric acid and DEHPA represents the 30%, 25% and 20% of the raw material cost, respectively.

The different incomes, expressed as percentage of total revenues for all the recycling processes, are provided in Fig. 8.

As it can be inferred from Fig. 8, there are three different revenues

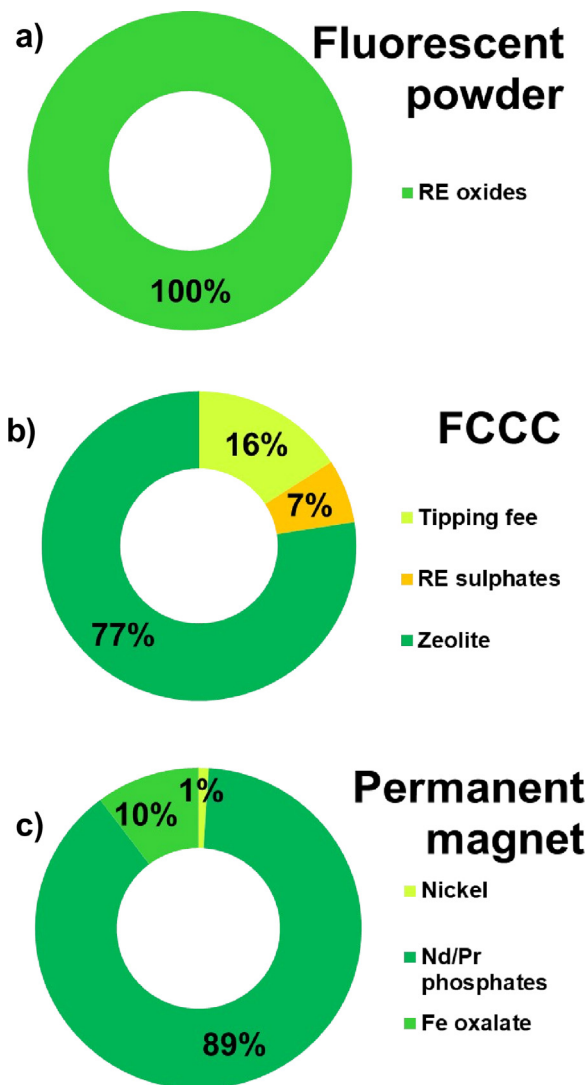


Fig. 8. Distribution of the revenues for each recycling process: a) fluorescent powder, b) FCCC, and c) permanent magnet.

for FCCC and permanent magnet recycling processes, whereas the sole revenue for the fluorescent powder process comes from selling of REO. Regarding FCCC, the main income is due to zeolite, that represents 77% of the total revenues, but 16% comes from the tipping fee; hence, RE sulphates account for only 7% of the total revenues, and this confirms that without the valorization of the leaching residue and a tipping fee such recycling process is extremely unprofitable. This is due to the very low concentration of lanthanum and cerium in the FCCC formulation.

On the other hand, for permanent magnets, neodymium and praseodymium salts represent by far the main income (89%), that could sustain the profitability of the process alone. Nonetheless, nickel and iron oxalate enhance the economic performance of the investment.

The indexes of profitability, calculated for the three baseline scenarios, are shown in Fig. 9.

The investment is profitable when the NPV is positive, and this condition is achieved in all the three cases. Nonetheless, for recycling of fluorescent powder the profitability is much lower than that of the other two processes. The DPBT is one year for the plants that treat fluorescent powder and permanent magnets; for FCCC, the same index is a higher, i.e. three years, that means that the sum of the discounted cash flows becomes positive after three years from the beginning of the activities. Thus, the performance of the FCCC recycling plant is the worst among those investigated. This is due to the greatest initial

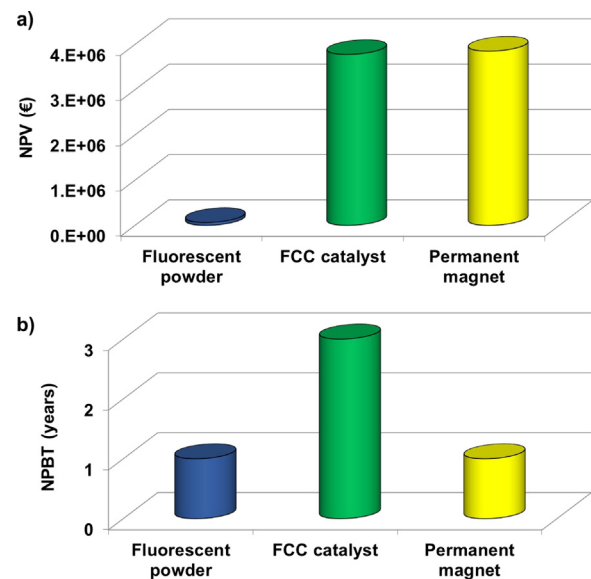


Fig. 9. NPV (a) and DPBT (b) calculated for the three processes.

investment charged on the FCCC project that implies a greater period to recover such investment. The profitability of the recycling plant for the treatment of permanent magnets is the most significant, according to the NPV index, and this was confirmed by the generated asset referred to the unit investment: the PI is indeed 1.26, 0.03 and 1.75 for FCCC, fluorescent powder and permanent magnets processes, respectively.

Data in Table 6 represent an essential information to evaluate the real advantage due to the implementation of the described processes. On the economic assessment basis, estimated by SuperPro software, the cost for kg of recovered metal is: 8.4 €/ton, 27.7 €/ton, 19.3 €/ton for the elements from fluorescent powders, FCCC and permanent magnets, respectively. Furthermore, the whole product cost is allocated on the market price, to assign a specific value to each recovered metal. The element price, referred to 2017, was chosen to assess the possible edge of the secondary production and it confirmed values in favor of the recycling treatments. According to the LCA results, La and Ce from FCCC represent an exception, with a recycling cost for kg around 6 times higher than the current oxide price on the market. Nevertheless, a significant economic load reduction is obtained thanks to a double aspect: the avoided FCCC disposal (around 250 €/ton) and the value of the 8500 t/year of produced zeolite, around 90–180 €/ton [48,107]. Furthermore, considering the significant advantage of the most secondary metals, the implementation of the three treatments within the same facility, combining the recovery of the different metals, could

Table 6

Comparison between the cost of metals from the described recovery processes and the price of the same elements from the primary production at 2017 [105].

Metal target	Cost of metal compounds from secondary production (€/kg)	Price of metal oxide from primary production (€/kg)
Fluorescent powder process		
Y	0.04	2.9
Eu	1.0	77.0
Ce	0.03	2.1
Gd	0.5	37.0
La	0.03	2.1
Tb	7.0	513.0
FCCC process		
La	14	2.1
Ce	14	2.1
Permanent magnet process		
Nd	8.0	57.0
Pr	11.0	74.0

**Table 7**

NPV (€) for the three recycling processes, considering revenues and operating costs  $\pm 10\%$  with respect to the baseline scenario.

	Scenario			
	A	B	C	D
FCCC	3200,000	11,000,000	– 5400,000	4400,000
Fluorescent powder	58,000	520,000	– 650,000	70,000
Permanent magnets	3500,000	5700,000	2000,000	4200,000

balance this difference with an overall increase of the economic sustainability.

#### 4.2.1. Alternative scenarios

The results of alternative scenarios are shown in Table 7. Those values confirm that the profitability is not always achieved when revenues and operating costs change with respect to those planned in the baseline scenario. In particular, scenario C (operating costs +10%, revenues –10%) is not profitable for the recycling plants of FCCC and fluorescent powder, as the NPV is negative and thus the DPBT is greater than 15 years, that is the project lifetime. This means that the costs are not recovered within the project lifetime.

For fluorescent powder, scenario C even entails that the annual operating costs are greater than revenues (+170,000 €/year), so that the profitability can never be achieved. On the other hand, under the hypotheses made in the study, the profitability is always achieved in the recycling of permanent magnets, since the revenues are, by far, greater than the operating costs of the baseline scenario.

## 5. Conclusions

The modern society has to face a double problem: the high waste amount to be managed, often classified as hazardous, and the need of REE supply for the manufacturing of the technological equipment, mainly in the renewable energy field.

Considering the relevant metal concentration within scraps, like fluorescent powders, end-of-life FCCC and permanent magnets, the scientific community has developed many processes for their exploitation, overlooking the sustainability aspects. In this regard, the present paper confirms the possible advantage derived from the production of REEs from waste from both the environmental and the economic point of view. In this regard the kg CO<sub>2</sub>-eq. gain can reach the 200 times, for the Eu from the fluorescent powders, compared to the primary production. In agreement with the environmental results, the secondary production shows a cost around 70 times lower than the primary supply. Furthermore, the sustainability assessment identified the main weaknesses of the FCCC treatment, which could be improved verifying the possibility of the substitution of sodium hydroxide, used for the pH adjustment agent. The profitability analysis confirmed the economic sustainability of the three processes under the assumed hypothesis for the baseline scenario. However, the assessment of the alternative scenarios highlighted that the market fluctuation of REE, energy and raw material prices might affect the profitability of both the fluorescent powders and the FCCC treatments. Overall, the analysis proved the significant advantage obtained thanks to the combination of the three processes within the same facility, correlating the sustainability aspects with the implementation of the circular economy pillars [108]. In this regard, the present work fits perfectly within the priority area of the European Circular Economy Action Plan related to the recovery of critical raw materials and it represents a concrete step towards the development of the innovative circular economy model. The worldwide applicability of the work represents the research strength, since the discussed issues concern not only the European territory and the possibility to develop minimum emission technologies is an essential step towards a low carbon transition.

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## Declarations of interest

None.

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